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Citation for published version:

Wang, X, Sanna, A, Maroto-Valer, MM & Paulson, T 2015, 'Carbon dioxide capture and storage by pH swing mineralization using recyclable ammonium salts and flue gas mixtures', *Greenhouse Gases: Science and Technology*, vol. 5, no. 4, pp. 389-402. <https://doi.org/10.1002/ghg.1494>

Digital Object Identifier (DOI):

[10.1002/ghg.1494](https://doi.org/10.1002/ghg.1494)

Link:

[Link to publication record in Heriot-Watt Research Portal](#)

Document Version:

Peer reviewed version

Published In:

Greenhouse Gases: Science and Technology

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Carbon dioxide capture and storage by pH swing mineralization using recyclable ammonium salts and flue gas mixtures

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Abstract: CO₂ mineral sequestration through the employment of silicate rocks such as serpentine is an important technology for the mitigation of CO₂ emissions. Most mineral carbonation works in this study use pure CO₂. The indirect carbonation process employed different flue gases (5, 15, 25% CO₂) and the presence of SO_x and NO_x. Also, the direct contact of CO₂ with the Mg source was compared to the indirect reaction of Mg with CO₂ as NH₄CO₃. The impact of variables such as temperature, solid-liquid ration (S/L), and molar ratio of additives on carbonation rate and degree was studied. An average carbonation efficiency of about 90% was achieved at 80°C after 30 min for indirect mineral carbonation process. The carbonation efficiency decreased to 50–60% when the process was directly employed. The carbonation efficiency obtained in the presence of 15–25% CO₂ was very similar to that with 100% CO₂ at 140°C, while at 80°C, the carbonation efficiency in presence of flue gas (40–55%) was much larger compared to that using pure CO₂ (10% after 3 h). SO_x and NO_x co-removal efficiency was 54.4% and 18% at 140°C and 20 bar, respectively.

Keywords: indirect mineral carbonation; flue gas mixture; NO_x; SO_x

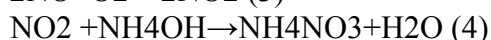
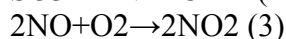
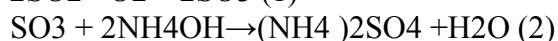
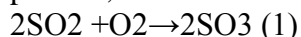
Introduction

Carbon dioxide capture and storage by mineralization (CCSM) is a promising strategy for permanently and safely storing anthropogenic CO₂ in solid magnesium (Mg) and calcium (Ca) carbonates. The advantages of CCSM include large storage capacity, worldwide availability feedstock, permanent and inherently safe sequestration of CO₂, and moreover it is an exothermic process. 1 However, mineral sequestration also faces barriers, such as low efficiency of mineral dissolution, slow kinetics, and energy intensive pre-treatment of the feedstocks. 2 O'Connor *et al.* 3 reported that mineral dissolution is the rate-limiting step in direct aqueous mineral carbonation, since the acidity produced by pressurized CO₂ in aqueous solution was not sufficient for mineral dissolution. Gadikota *et al.* recently reported the NaCl and NaHCO₃'s role to maintain the pH in the system of single-step serpentine mineralization. 4 The results indicated that the high carbonation conversion can be obtained without a pH-swing process. However, this needs to be further investigated. In order to improve the carbonation conversion, pH-swing processes have been proposed, where the carbonation of the leached solution was promoted by using a basic medium. Park *et al.* 5 proposed a pH swing process using mixed weak acid solvents with 1 vol% H₃PO₄, 0.9 wt% of oxalic acid and 0.1 wt% EDTA (ethylenediaminetetraacetic acid) to promote mineral leaching. Nesquehonite (MgCO₃·3H₂O) was obtained from the carbonation of a Mg-rich solution by raising the pH of the solution to 9.5 with NH₄OH. The overall conversion to

MgCO₃ was ~65%. However, the additives used in Park's process were not recycled and the dissolution efficiency was around 70%. Teir *et al.* 6 dissolved serpentine in HCl or HNO₃, and then hydromagnesite (4MgCO₃ · Mg(OH)₂ · 4H₂O) was obtained by controlling the Mg-rich solution pH to 9 with addition of NaOH. 7 Although high carbonation conversion efficiency of Mg (80–90%) was obtained, the chemicals involved, such as HCl and NaOH, could not be reused. For Teir's process, 2.4 t NaOH and 2.1 t HCl acid (or 3.6 t HNO₃) were consumed per tonne of CO₂. As a consequence, the cost for make-up chemicals alone (600–1600 US\$/t CO₂) was much larger than the budget for CO₂ emission allowances (30–40 US\$/t CO₂). 8 Thus, recycling of all chemicals involved is crucial to make CO₂ mineral carbonation a viable process.

Krevor *et al.* 9 reported the use of 0.1 M of NH₄Cl, NaCl, sodium citrate, sodium EDTA, sodium oxalate, and sodium acetate to dissolve serpentine at 120°C and 20 bars of CO₂ in a batch autoclave. They achieved 60% dissolution efficiency of Mg from serpentine within 2 h, rising to 80% after 7 h and reaching nearly 100% between 10 and 20 h. Therefore, the mineral dissolution with organic solvents was promising in terms of dissolution efficiency, but unfortunately, the dissolution rate was relatively slow and needed a long reaction time of up to 20 h. A novel CCSM process with recyclable ammonium salts has been reported by Wang and Maroto-Valer 10 to overcome these barriers. This process integrates mineral carbonation with CO₂ capture by employing NH₃, NH₄HSO₄, and CO₂ containing ammonium salts in the capture, mineral dissolution, and carbonation steps, respectively. The NH₄HSO₄ and NH₃ can then be regenerated by thermal decomposition of (NH₄)₂SO₄, which is the by-product from the process. The use of CO₂ containing ammonium salts as the source of CO₂ can avoid desorption of CO₂, which account for 70% of the total energy consumption in the whole CCS chain. They reported that at 100°C 1.4 M NH₄HSO₄ extracted 100% of Mg from serpentine in 3 h, as well as 98% of Fe and 17.6% of Si. 11 The mechanism of dissolution and effect of temperature and time were also investigated.

The rate-limiting mechanism of serpentine dissolution with NH₄HSO₄ is a chemical reaction with product layer diffusion control and the activation energy of this dissolution was 40.9 kJ mol⁻¹. 11 Wang and Maroto-Valer 12 also demonstrated that 95% of carbonation efficiency could be achieved at 85°C in 1 h, if the mass ratio of Mg/NH₄HCO₃/NH₃ is 1:4:2. Similar carbonation efficiency was achieved in presence of 50/50 mixture of NH₄HCO₃ and (NH₄)₂CO₃. Temperature, concentration of additives and reaction time, have been reported to affect significantly carbonation efficiency. 13 However, other variables may provide an opportunity to optimize the mineralization process. For example, CO₂ sequestration directly from flue gas by aqueous mineral carbonation has not been investigated. Moreover, the simultaneous removal of SO_x and NO_x has received very little attention thus far. Recently, Yan *et al.* 14 reported a CO₂ carbonation efficiency of ~20% when SO_x and NO_x were present in the flue gas (15% CO₂) using wollastonite at 40 bar and 150°C. Accordingly, in this work the carbonation rates of serpentine in pure CO₂ and several simulated flue gases were investigated. It is proposed that for direct flue gas mineralization using the ammonia process, SO_x and NO_x can be removed by ammonia according to following reactions:



Therefore, experimental work was carried out to quantify the SO_x and NO_x removal efficiency in direct flue gas mineralization.

Experimental method

A carbonation parametric study was conducted using an 8 g/L Mg^{2+} aqueous synthetic solution (prepared using $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) to keep the same initial concentration for different bench of carbonation experiments. The synthetic Mg^{2+} solution is representative of a solution from a dissolution experiment, where 8 g/L is the average level of Mg concentration from 75 to 150 μm serpentine particles dissolution with 1.4M NH_4HSO_4 at 100°C for 1 h (50 g/L).¹¹ The main difference between the synthetic solution and that coming from the dissolution experiments is the presence of impurities, such as Ca, Fe, Ni, and other metal cations that are found in naturally occurring minerals and will not be present in the synthetic solution. However, the concentration of these is lower than 30 ppm.¹¹ The Mg-containing samples with particle size 75–150 μm , provided by the British Geological Survey (BGS), included serpentinites from the Ballantrae area (samples ET5 and ET6), and from the Portsoy area (samples ET11 and ET13). Two sets of experiments were performed: (i) carbonation experiments with the reaction of MgSO_4 (Mg from the dissolution of silicate rocks) and $(\text{NH}_4)_2\text{CO}_3$ / NH_4HCO_3 (mixture of salts resulting from the capture of CO_2 with NH_3); (ii) carbonation of MgSO_4 directly with pure CO_2 or mixtures containing 5, 15 and 25% v/v CO_2 balanced with N_2 , where the mixtures simulated the gas emission from natural gas processing, power plant and cement/steel industries, respectively. The ammonium salts, $(\text{NH}_4\text{HCO}_3$ and $(\text{NH}_4)_2\text{CO}_3$, 50/50 mixture of them) were used to represent the intermediate products from the aqueous ammonia CO_2 capture (absorption step only). Kim¹⁵ reported that the mixture of NH_4HCO_3 and $(\text{NH}_4)_2\text{CO}_3$ with a molar ratio of 1:1 was obtained from the absorption step of aqueous ammonia capture, where 13% w/w NH_3 water was used to capture 15% of CO_2 . NH_3 water was added to improve the carbonation efficiency as previously reported.¹² The amount required was determined considering a molar ratio of $\text{Mg}:\text{NH}_3$ of 1:2. Both pressurized and unpressurized reactor systems were used in this study. Both of them allow online sampling. The systematic diagrams of un-pressurized and pressurized system are presented in previous work^{11,13} as seen in Fig. 1. The experimental procedure for each experiment was as follow: i. An 8 g/L Mg^{2+} solution 200 mL (mimics 50 g/L solid-liquid ratio dissolution, 80% Mg dissolution efficiency) was prepared. ii. Ammonium salts and ammonia water were added into the solution, according to the ratio determined (no ammonium salts for CO_2 gas experiment), and the pH was measured using pH meter. iii. The system was sealed; then the CO_2 gas was injected (the initial pressure injected was 30 bara; the pressure dropped due to the uptake of CO_2 in solution and stabilized to 20 bara during experiments). There was no gas injection in experiments with ammonium salts. iv. Solutions were heated to a set temperature. Timing started when the set temperature was reached. v. The liquid was sampled at intervals (5, 10, 15, 30, 60, 120, and 180 min), and then the samples were analyzed by ICP-MS to determine the change of Mg concentration. vi. At the end of the experiments, the heating was stopped and the system was cooled down. After opening the reactor, the pH was measured immediately. vii. Finally, the precipitates from the slurry were filtered using a vacuum pump. The solids were then dried in an oven at 80°C for 24 h and analysed by XRD and SEM. Table 1 lists the 22 experiments (Exps) completed in this study. For experiments with CO_2 gas (Exps C1–C5 and Exps C15–C17), different concentrations of CO_2 gas were used to investigate the effect of flue gas composition on carbonation efficiency. Both 80°C and 140°C were used to investigate the effect of temperature on carbonation with CO_2 gas. For experiments with ammonium salts (Exps C6–C11), different molar ratios of $\text{Mg}:\text{ammonium salts}:\text{NH}_3$ were used to find the optimized ratio with highest carbonation efficiency. In the pressurized system, the evaporation of $\text{NH}_3/\text{NH}_4\text{HCO}_3/(\text{NH}_4)_2\text{CO}_3$ was prevented so that the consumption of additives could be reduced. Experiment 10 used 100°C to investigate the

effect of temperature on carbonation with ammonium salts. Experiment C13 was operated in an unpressurized system. Experiment C14 used 16g/l Mg²⁺ solution (which mimic 100g/L solid-to-liquid (S/L) ratio in dissolution) to investigate the effect of the S/L ratio on carbonation with ammonium salts. Experiments C12 and C18–22 used solution from the dissolution of UK resources to quantify the carbonation efficiencies. Both 80°C and 140°C were used to investigate the effect of temperature on carbonation with flue gas mixture (Exps C23 and C24). The carbonation efficiency was calculated using Eqn (5):

$$\text{Carb.\%} = (\text{Mg conc. Initial} - \text{Mg conc. measured by ICP-MS}) / 8000 * 100\% \quad (5)$$

where Mg concentration is in unit of ppm and 8000 represents the initial Mg concentration (ppm) in the parent serpentine sample. SO_x and NO_x co-carbonation experiments were carried out using a synthetic gas having a composition of 15% v/v CO₂, 1000 ppm SO₂, 500 ppm NO and 4% v/v O₂ used to mimic real flue gas. A model solution was prepared based on the dissolution experiments after pH-swing. The reaction conditions were selected as 80°C or 140°C, 30 bara, Mg:NH₃ molar ratio of 1:2, and 1 h duration, and were consistent with the previous carbonation experiments. Calibration experiments were conducted firstly to find the maximum uptake of SO_x and NO_x (more NH₃ was added with a long reaction time, assuming 100% removal of SO_x and NO_x). Then, experiments were carried out at 80°C and 140°C, respectively, to investigate the SO_x and NO_x removal efficiency compared to calibration. Liquid samples were taken before and after experiments in order to measure the anion concentration of nitrite and sulfate by Ion Chromatography. The SO_x and NO_x removal efficiency was determined by the following equation: SO_x/NO_x removal efficiency = concentration difference of sulfate or nitrate between before after experiments / concentration of sulfate or nitrate in calibration

Results and discussion

Effect of CO₂ concentration and ammonium salts

Figure 2 presents the variation of the carbonation efficiencies with time (Exps 1–17). A fast carbonation stage after 5 min was found in the carbonation experiments with both ammonium salts and CO₂ gases. The carbonation rate in the fast carbonation stage can be calculated by Eqn (6).

$$\text{Carbonation rate} = \frac{(M_{\text{mgi}} - M_{\text{mgi}})}{V \times (t_i - t_j)}$$

According to the calculation, the carbonation rate with ammonium salts was in the range of 4.4×10^{-4} to 9.4×10^{-4} mol/(l·s) during the first 30 min. The carbonation rate with CO₂ gas was in the range of 1.1×10^{-4} to 4.5×10^{-4} mol/(l·s). It can be seen that carbonation with ammonium salts (Fig. 2 blue color) has better kinetics than that with CO₂ gas (Fig. 2 pink color).

Regarding the carbonation efficiency, carbonation with ammonium salts showed 70–97% carbonation efficiency after 3 h and 62–94% after 30 min. Carbonation with CO₂ gas showed 13–67% carbonation efficiency after 3 h and 10–37% after 30 min. The better carbonation rate and efficiency with ammonium salts can be explained as follow. In CO₂ gas experiments, the injected CO₂ needs to first dissolve in water, and the CO₂ (l) will dissociate into HCO₃⁻ at pH above 6, and HCO₃⁻ can further dissociate into CO₃²⁻ at pH above 9. In the ammonium salts experiments, the alkaline NH₄HCO₃ and (NH₄)₂CO₃ can hold the pH above 8 in carbonation, and the HCO₃⁻ and CO₃²⁻ are dissociated from NH₄HCO₃ and (NH₄)₂CO₃ directly, avoiding CO₂ dissolution and dissociation. 12

Figure 3 presents the carbonation efficiencies for different times using different concentration of CO₂; where a Mg to NH₃ ratio = 1:2 was used. It is found that carbonation efficiency

increases with the increase of CO₂ concentration at both 80°C and 140°C. Although diffusion of CO₂ in solution is the controlling limit in carbonation, two exceptions have been found in the experiments. The first exception happened at Carbonation experiment with 100% CO₂ at 80°C, since the acidity of high CO₂ decreases pH significantly and the carbonation is unfavorable at low pH condition. The acidic change with CO₂ composition needs to be considered. The pH value was around 10.0 before carbonation; it dropped to 6.1 after carbonation when 100% CO₂ was used compared to 7.5–8.5 for the experiments carried out with 5–25% CO₂ gas. The second exception happened at experiment with 140°C and 100% CO₂, the carbonation efficiency did not show any further increase compared to the experiment carried out with 25% CO₂. Since rising temperature decreases the solubility of CO₂, the solubility change of CO₂ with temperature needs to be considered. Therefore, the carbonation behavior with diluted CO₂ gas is different to that in presence of pure CO₂ gas. Also, for pure CO₂ carbonation, a high temperature (140°C) is required.

Temperature

Figure 4 presents the carbonation efficiencies for different times using different temperatures; 80°C and 140°C were used for CO₂ gases, and 80°C and 100°C were used for ammonium salts. It was found that the carbonation efficiency increases with the increasing temperature in both CO₂ gas and ammonium salts carbonation runs. Power *et al.* also reported the serpentine carbonation increasing with the rising of temperature. [17] This is consistent with the rule of exothermic reaction, where the reaction rate is temperature dependent. For carbonation with CO₂ gases, 140°C is favorable. Differently, in the carbonation experiments with ammonium salts, there is not much difference for different temperatures with 80°C being slightly favorable.

Mg: ammonium salts: NH₃ 3 ratio

Figure 5 presents the carbonation efficiencies at different times using different ratios of Mg: ammonium salts: NH₃, where 80°C, 8 g/L Mg solution, and an autoclave reactor were used. The ratio of Mg: ammonium salts: NH₃ ratio determines the amount of additives used. In previous work, the carbonation efficiency could reach 96% when Mg: ammonium salts: NH₃ ratio was 1:4:3 (Wang and Maroto-Valer, 2011c). However, the stoichiometric ratio for carbonation with NH₄ HCO₃ is 1:1:1. Too many additives were used to get high efficiency. Reducing the amount of additives can save energy consumption in the chemical recycling step. But the carbonation efficiency is affected by the amount of additives. Careful selection of ratio is needed. From this study, it is found that using a pressurized reactor (3 bara resulted from ammonia vapor) can reduce the loss of ammonia and therein reduce the amount of additives. In the pressurized reactor, 70% carbonation efficiency was reached at 30 min, so the reaction rate at a pressurized reactor is faster than that at an unpressurized reactor: 80% and 93% efficiencies were achieved in 60 min at a ratio of 1:2:1 and 1:2:2, respectively. Further reduction of additives can be achieved by increasing the pressure. Maximum pressure from ammonia vapour is 3 bara, so steam injection can be used to increase the pressure to higher level.

Comparison of a synthetic MgSO₄ solution and a solution from dissolution of UK serpentinite resources

Figure 6 presents the carbonation efficiencies at different times using a synthetic solution (8 g/L Mg) and a solution from dissolution experiments. The synthetic solution was prepared with MgSO₄·7H₂O and Millipore water. The Mg concentration of solution was 8 g/L, which is representative for 80% of dissolution efficiency at 100°C, 1.4 M NH₄HSO₄ and 1 h. The solution from the dissolution experiment was obtained by using 1.4 M NH₄HSO₄ reacted

with sample ET16 for 1 h at 100°C. After dissolution, ammonia water was added into the solution to increase the pH to a value of 7 and some of impurities, mainly Fe, Cu, Zn, and Ni, were precipitated. After pH-swing, the Mg concentration of the solution from the dissolution experiments was in the range of 6–9 g/L. Carbonation experiments with these two solutions were carried out at 80°C, Mg: ammonium salts: NH₃ ratio as 1:1:2, using a pressurized reactor. A 71% carbonation efficiency was achieved using the solution from the dissolution of serpentinite, while a 77% efficiency was obtained with the synthetic solution. The difference is due to the presence of impurities in the dissolution solution, such as Fe, Ca, Mn, and Co. These impurities can also react with CO₂ to produce carbonates. However, the carbonation efficiency calculation used in this study only considered Mg carbonation, but the excluded elements could contribute to the total amount of CO₂ captured. Another difference between these two solutions is (NH₄)₂SO₄ presented (NH₄HSO₄ convert to (NH₄)₂SO₄ in dissolution and pH swing steps) in solution from the dissolution stage. After the addition of NH₃ water, NH₄⁺–NH₃ buffer solution can be formed. The buffer solution can help to prevent a pH drop and the carbonation can benefit from this.

Solid-to-liquid ratio

Increasing the S/L ratio from 50 to 100 g/L, the size of the carbonation reactor, and water usage are reduced by 50%. However, the data shown in Figure 7 demonstrate that increasing the solid content to 100 g/L only lowers the carbonation efficiency from 97% to 90%. Any further increase of S/L at 100°C is impossible, since MgSO₄ exceeds its solubility and precipitates out from the solution. The maximum S/L is dependent on the dissolution efficiency of Mg. If an average of 80% dissolution efficiency is taken into consideration, the maximum S/L ratio is around 130 g/L. Besides, rising the operation temperature can further increase the MgSO₄ solubility.

UK resources

The carbonation experiments obtained using real solutions from the dissolution of UK Mg-silicate resources conducted at 80°C with an Mg: ammonium salts:NH₃ ratio of 1:2:2 for 1 h using a pressurized reactor (3–4 bara resulted from ammonia vapor) are presented in Fig. 8. The carbonation efficiency is close to 90% and the data is in agreement with the experiments using the synthetic solution (95%). The red circle indicates that a 30-min reaction is enough to obtain the highest carbonation efficiency. Similar efficiency is obtained using different Mg-silicates from different UK locations.

Reaction products characterization

Seven samples of the carbonation product were provided by the University of Nottingham and analyzed by means of SEM and XRD at the British Geological Survey (BGS). The carbonation reactions were conducted under varied conditions of temperature and source of CO₂. The temperatures ranged from 80 to 140°C. The CO₂ was derived from CO₂ balanced with nitrogen as a representative for gas emission from industry and from an ammonium source, NH₄HCO₃ and (NH₄)₂CO₃. The analyses revealed that although compositionally similar, the samples display significant differences in crystal morphologies and therefore they are described separately. The XRD analysis (Table 2) revealed that most of the samples analyzed are composed dominantly of hydromagnesite, however minor amounts of other phases were also identified and are listed below along with their chemical formula. Overall, hydromagnesite accounts for over 90% indicating that a high purity product can be obtained. The crystal habit was platy anhedral to subhedral, diaphanous sheet-like or wispy, while the crystals form was spherical, nest-like, sometimes elongated aggregates. This morphological diversity reflects the differences in the experimental parameters, such as temperature,

concentration ratio of Mg:ammonium salts:ammonia, source of carbon. Product C3 (Fig. 9 (a)) (Carbonation conditions: 25% CO₂, 80°C) was a very fine powder composed mainly of hydromagnesite (Mg₅(CO₃)₄(OH)₂·4H₂O) (96%) and minor amounts of hexahydrite (MgSO₄·6H₂O) (2.3%), hydrotalcite (Mg₆Al₂CO₃(OH)₁₆·4(H₂O)) (1%) and dypingite (Mg₅(CO₃)₄(OH)₂·5H₂O) (0.7%). The crystals were fine and exhibit platy to sheet-like habit, 10 µm in diameter and 1 µm in thickness. The crystals were usually aggregated into bundles. The crystal arrangement is both random and ordered and resembles a rosette-like fabric. Product C7 (Fig. 9 (b)) (Carbonation conditions: Mg:NH₄HCO₃:NH₃ 1:2:2, 80°C) comprises an infinite number of rod-like particles. These particles are typically <25 µm long and <5 µm wide and are composed of randomly oriented crystals of hydromagnesite. The crystals exhibit a range of sizes but usually do not exceed 3 µm in diameter and 300 nm in length. The morphology is dominated by sheets and diaphanous. Product C8 (Fig. 9 (c)) (Carbonation conditions: Mg:ammonium salts:NH₃ 1:2:2, 80°C) particles morphology is dominated by spheres that frequently are mutually attached forming aggregates. Sample C12 (Fig. 9 (d)) crystals form diaphanous sheets that vary in size from <1 µm to ca. 15 µm, which for an overall spherical shape. Sample C14 (Fig. 9 (e)), which represents the carbonation product from the 100g/L S/L ratio experiments, was wholly composed of hydromagnesite. The crystals of this sample are sheet-like and usually < 5 µm. The sheets are often circular and arranged into dense spherical aggregates. The carbonation product obtained at 140°C in the presence of 55% CO₂, (Sample C16, Fig. 9 (f)) is composed predominantly of hydromagnesite (87.1%) in form of rosette-like aggregates of platy crystals. Finally, crystals from sample C17 (Fig. 9 (g)), which represent the product obtained at 140°C in presence of 25% CO₂, have a sort of rhombohedral shape aggregates in a variety of different forms, such as cross-like, nest-like, or flattened spheres. The analysis of the Mg and CO₂ ratio were used to give indication of the different hydromagnesite form precipitated. 5MgO·4CO₂·5H₂O/Mg/CO₂ presents an mg/CO₂ ratio of 1.25. The Mg/CO₂ ratio was found to be between 1.00 and 1.20 (for the samples C6–C12 which represented the experiments run with ammonium salts and CO₂ at 140°C. The Mg/CO₂ ratio was instead 0.96 (C3) for the experiment run with CO₂ gas at 80°C. The products from our experiments were a mix of different formation of hydromagnesite: (i) the mix of 5MgO·4CO₂·5H₂O and 5MgO·5CO₂·4H₂O was the products from carbonation using ammoniums salts; (ii) the mix of 3MgO·4CO₂·5H₂O and 5MgO·5CO₂·4H₂O was the products from carbonation using CO₂ gas at 80°C; and (iii) the mix of 4MgO·2CO₂·5H₂O, 5MgO·2CO₂·7H₂O and 5MgO·4CO₂·5H₂O was the products from carbonation using CO₂ gas at 140°C. The particle size distribution of products from carbonation experiments is presented in Fig.10. The d₉₀ were reported as 92 and 98 µm for 1 h and 3 h, respectively. The main user of carbonates from CCSM would be the construction industry where the options for use without release of CO₂ are in the form of pulverized powder (<300 µm) for fillers. Other applications such as PCC quality where the particle size distribution (diameter <2 µm) would require further post-processing to meet the application criteria and purity limits. 18

SO_x and NO_x removal in direct flue gas mineral carbonation

The SO_x removal efficiency was 41.6% and 54.4% at 80°C and 140°C, respectively, indicating that the removal of SO_x can be enhanced by an increase of temperature. In contrast, NO_x removal efficiency was 24.4% and 17.8% at 80°C and 140°C, respectively. The low removal efficiency of SO_x and NO_x was associated with inadequate oxidation of NO and SO₂, since NO and SO₂ cannot directly react with NH₃. The 4% v/v oxygen content in flue gas was not enough to convert NO/SO₂ to NO₂/SO₃. In order to maximize the SO_x and NO_x removal in direct flue gas mineralization, an oxidation step using oxidation agents typically employed in water treatment (e.g. ozone, H₂O₂, UV-light) need to be added before

the removal step. The carbonation efficiency decreased from 36.3% and 46.6% to 25.6% and 33.2% at same temperature and CO₂ content conditions, respectively (Table 3). Because, the low carbonation efficiency can derive from the increase of solution acidity in presence of SO₂ and NO, which inhibits the generation of carbonate precipitate and from competition reactions on Mg²⁺ ion in the solution. 14

Conclusions

In summary, an average Mg carbonation with ammonium salts of about 90% was achieved at 80°C, 30 min, Mg:ammonium salts:NH₃ ratio as 1:2:2 and a solid to liquid ratio of 50 g/L, and an average Mg carbonation of about 55% was achieved at 140°C, 60 min, Mg:NH₃ ratio as 1:2 and a solid to liquid ratio of 50 g/L with 100% and 25% CO₂ gas. Carbonation with ammonium salts is better than that with CO₂ gas. However, rising CO₂ concentration (5–25%) can increase carbonation efficiency, but 100% CO₂ behave low pH thus decrease carbonation efficiency significantly. Besides, carbonation using pressurized reactor is better than that using an unpressurized reactor due to the prevention of additives loss. An increased S/L ratio from 50 to 100 g/l can reduce by 50% the size of the carbonation reactor. Moreover, the mineral carbonation can also remove SO_x and NO_x, the experiments showed that 54.4% SO_x removal efficiency and 24.4% NO_x removal efficiency were achieved at 80°C, respectively.

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Figures

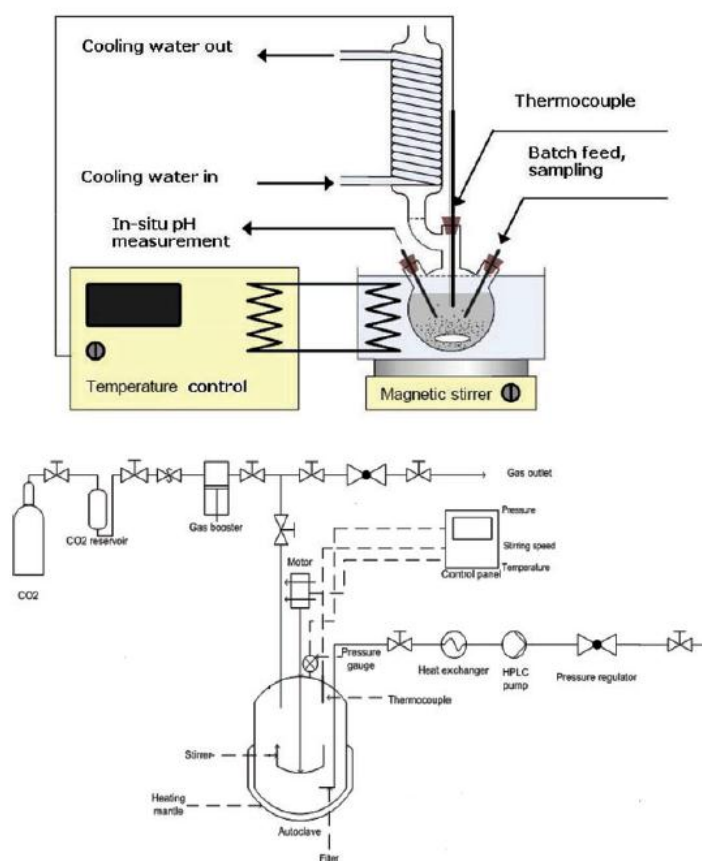


Figure 1. Unpressurized (a) and pressurized system (b).

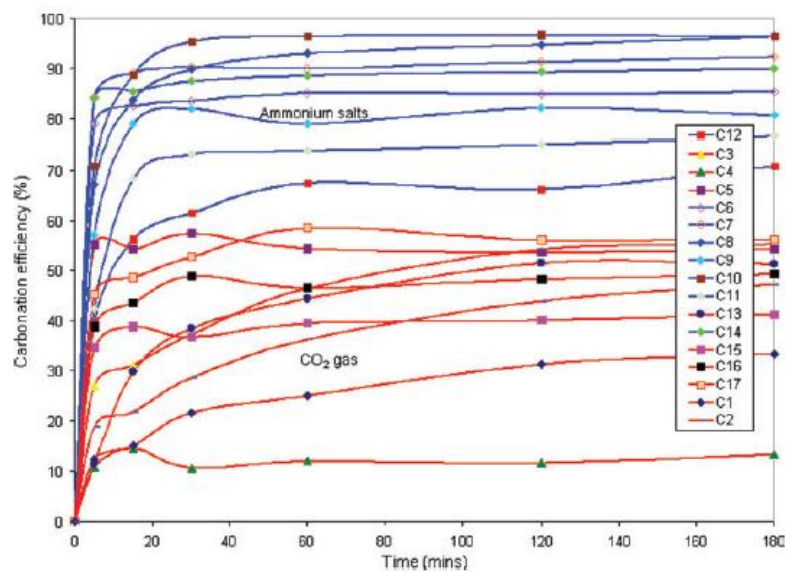


Figure 2. Carbonation efficiency vs. reaction time for all experiments.

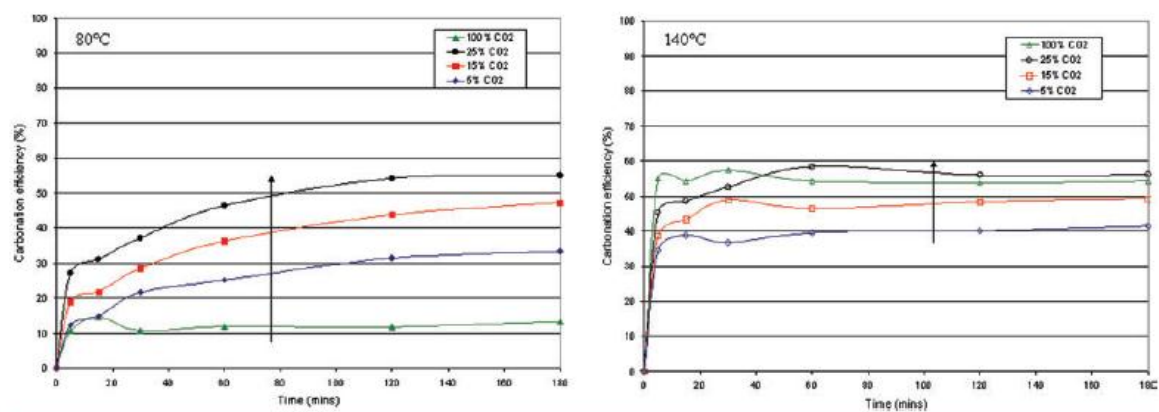


Figure 3. 80°C (a) and 140°C (b) CO₂ gas experiments at different concentrations of CO₂.

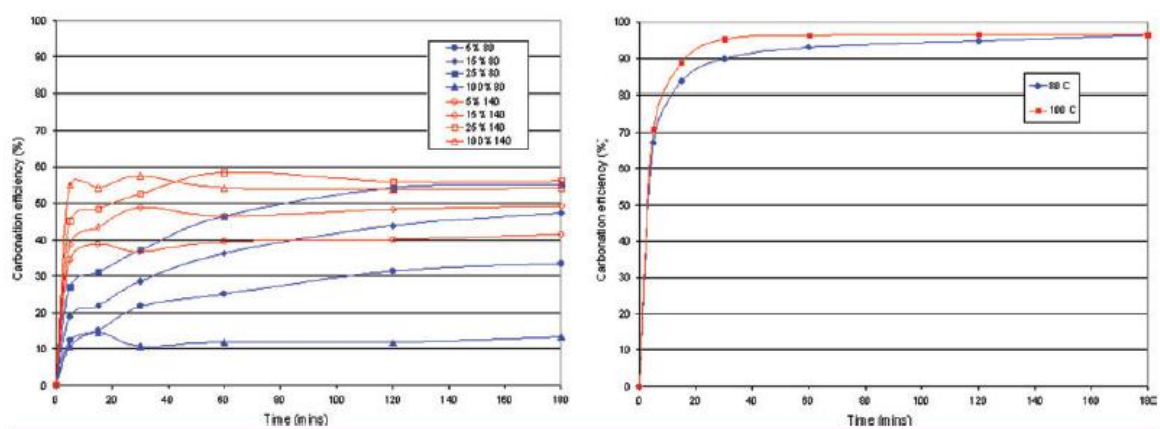


Figure 4. CO₂ gas (a) and ammonium salts (b) carbonation experiments at different temperatures.

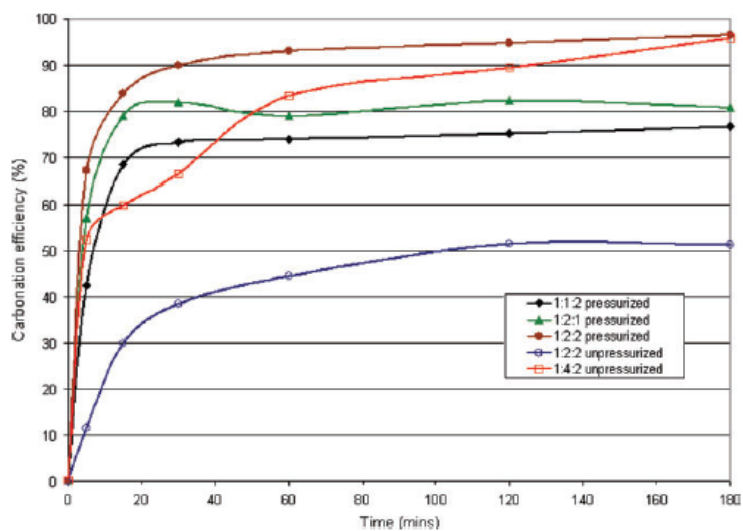


Figure 5. Carbonation efficiency at different Mg:ammonium salts:NH₃ ratios.

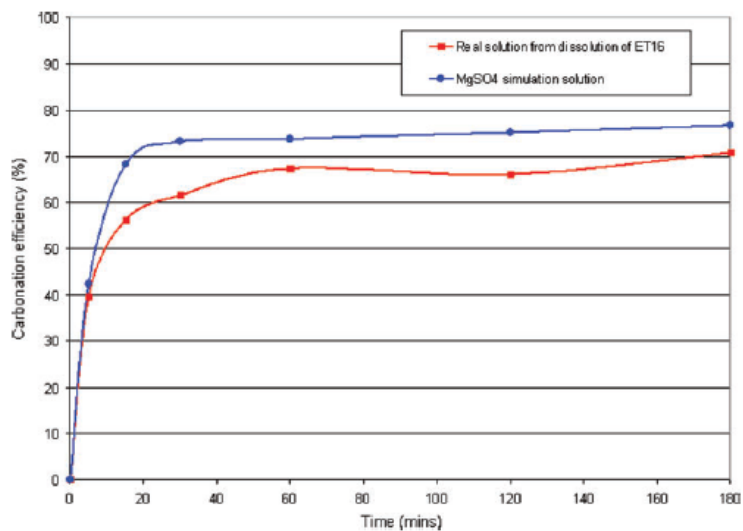


Figure 6. Carbonation efficiency using synthesis and solution from dissolution experiments of UK resources.

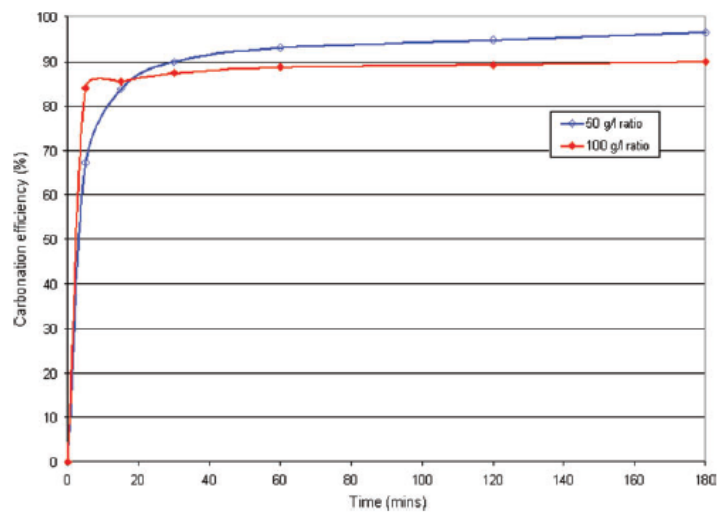


Figure 7. Carbonation efficiency at different solid-liquid ratios.

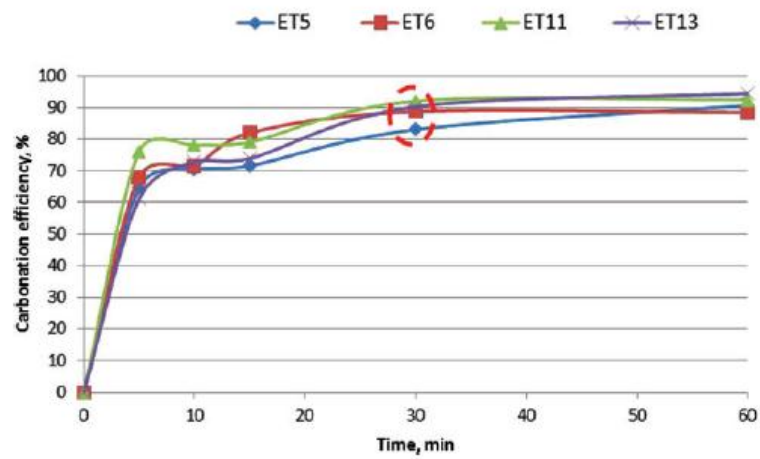


Figure 8. Carbonation efficiency using solutions from dissolution of different UK resources.

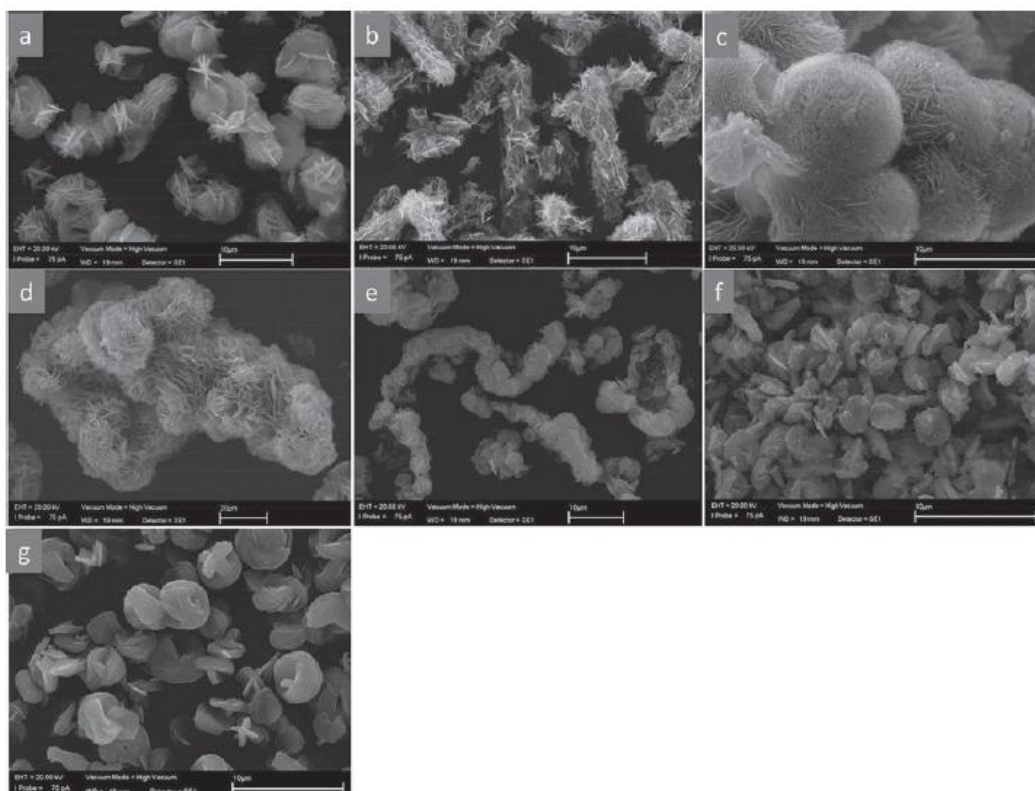


Figure 9. SEM photomicrographs showing the crystals formed during carbonation. Image (a) C3; (b) C7; (c) C8; (d) C12; (e) C14; (f) C16; (g) C17.

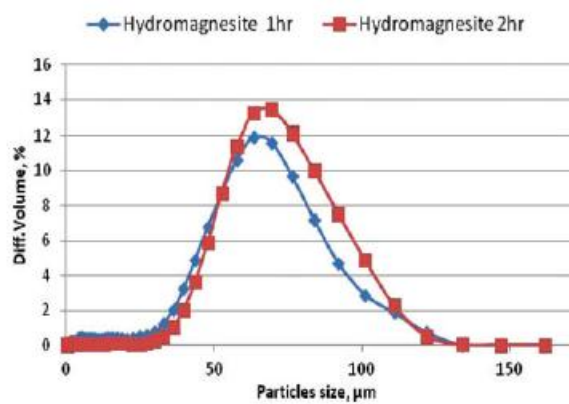


Figure 10. Particle size distribution of products from carbonation experiments.

Tables

Table 1. Carbonation experiments conducted in this work.

Run	Solution	CO ₂ source	T(°C)	P (bara)	T (h)
C1	8000 mg/l Mg ²⁺ 200 ml	5% CO ₂	80	20	3
C2	8000 mg/l Mg ²⁺ 200 ml	15% CO ₂	80	20	3
C3	8000 mg/l Mg ²⁺ 200 ml	25% CO ₂	80	20	3
C4	8000 mg/l Mg ²⁺ 200 ml	100% CO ₂	80	20	3
C5	8000 mg/l Mg ²⁺ 200 ml	100% CO ₂	140	20	3
C6	8000 mg/l Mg ²⁺ 200 ml	M* = 1:2:2	80	2	3
C7	8000 mg/l Mg ²⁺ 200 ml	M = 1:2:2	80	2	3
C8	8000 mg/l Mg ²⁺ 200 ml	MA** = 1:2:2	80	2	3
C9	8000 mg/l Mg ²⁺ 200 ml	MA = 1:2:1	80	2	3
C10	8000 mg/l Mg ²⁺ 200 ml	MA = 1:2:2	100	3	3
C11	8000 mg/l Mg ²⁺ 200ml	MA = 1:1:2	80	1	3
C12	Solution ET16 200 ml	MA = 1:1:2	80	1	3
C13	8000 mg/l Mg ²⁺ 200 ml	MA = 1:2:1	80	N/A	3
C14	16000 mg/l Mg ²⁺ 200 ml	MA = 1:2:2	80	3	3
C15	8000 mg/l Mg ²⁺ 200 ml	5% CO ₂	140	20	3
C16	8000 mg/l Mg ²⁺ 200 ml	15% CO ₂	140	20	3
C17	8000 mg/l Mg ²⁺ 200 ml	25% CO ₂	140	20	3
C18	Solution ET5 200ml	MA = 1:2:2	80	2	1
C19	Solution ET6 200 ml	MA = 1:2:2	80	2	1
C20	Solution ET11 200 ml	MA = 1:2:2	80	2	1
C21	Solution ET13 200 ml	MA = 1:2:2	80	2	1
C22	Solution ET5 200 ml	MA = 1:2:2	80	2	1
C23	8000 mg/l Mg ²⁺ 200 ml	Flue gas mixture	80	2	1
C24	8000 mg/l Mg ²⁺ 200 ml	Flue gas mixture	140	2	1

*M indicates the value of Mg: (NH₄)₂CO₃:NH₃

**MA indicates the value of Mg: Ammonium salts:NH₃, where ammonium salts is the mixture of NH₄HCO₃ and (NH₄)₂CO₃ with 1:1 molar ratio.

Table 2. Mineralogy of products from carbonation experiments.

Experiment number	Mineralogy (%)				
	Brucite Mg (OH) ₂	Hexahydrite MgSO ₄ 6H ₂ O	Hydromagnesite Mg ₅ (CO ₃) ₄ (OH) ₂ 4(H ₂ O)	Hydrotalcite Mg ₅ (CO ₃) ₄ (OH) ₂ 5(H ₂ O)	Lizardite Mg ₃ Si ₂ (OH) ₄ O ₅
C3		2.3	96	1	0.7
C7			100		
C8			100		
C12		2.9	96.5	0.6	
C14			100		
C16	10.2		89.6	< 0.5	
C17			98.6	1.4	

Table 3. Carbonation efficiency, SO_x removal efficiency and NO_x removal efficiency with 15% CO₂ at 80°C and 140°C.

	Carbonation efficiency	SO _x removal efficiency	NO _x removal efficiency
C2	36.3%	N/A	N/A
C16	46.6%	N/A	N/A
C23	25.6%	41.6%	24.4%
C24	33.2%	54.4%	17.8%